



(11) Publication number : **0 636 687 A2**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number : **94305448.6**

(51) Int. Cl.<sup>6</sup> : **C11D 3/37**

(22) Date of filing : **22.07.94**

(30) Priority : **30.07.93 GB 9315854**

(43) Date of publication of application :  
**01.02.95 Bulletin 95/05**

(84) Designated Contracting States :  
**BE DE FR GB IT NL**

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(54) Improvements in or relating to hydrotropes.

(57) An aqueous composition, such as a household, industrial or institutional cleaning product, comprises electrolyte, surfactant and polymeric hydrotrope. The polymer preferably comprises (meth) acrylic acid and styrene, with a molecular weight in the range 1,000 to 1,000,000, and is substantially non cross-linked.

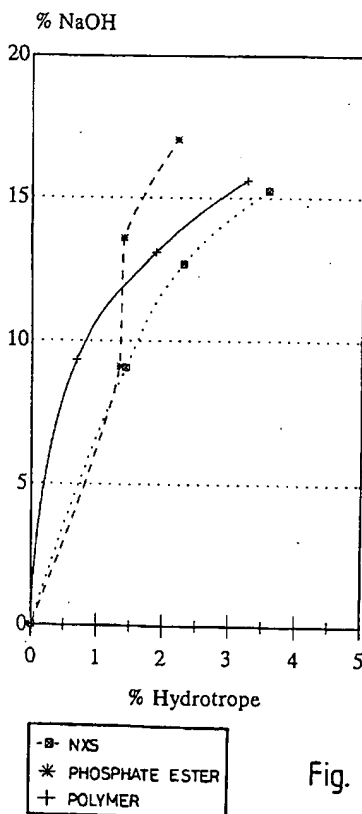


Fig. 3

Field of Invention

This invention concerns hydrotropes (or hydrotropic agents), ie substances which will solubilise a surfactant in an aqueous solution of an electrolyte without significantly altering the surface active properties of the surfactant, and relates to a novel class of hydrotropes and their use in aqueous compositions, particularly cleaning compositions.

Background to the Invention

Many liquid cleaning products contain electrolytes (such as phosphates, silicates, hypochlorites etc), and also surfactants, which are typically included for their detergency and wetting properties. Many surfactants are insoluble in the electrolytes at the concentrations used, and hydrotropes are employed to assist in the formulation and stabilisation of many liquid cleaning products. For example, hydrotropes are currently used in products such as liquid detergents, multi-surface cleaners, automatic and manual dishwashing detergents, and all-purpose cleaning products.

Hydrotropes are generally low molecular weight compounds, often with an amphiphilic character, having both hydrophilic and hydrophobic functional groups. Examples of materials currently used as hydrotropes include sodium xylene sulphonate (SXS or NXS), phosphate esters and alkyl polyglycosides.

For further information on hydrotropes see, for example, J. Dispersion Science and Technology, 9 (5 + 6), 443-457 (1988-89), J. Dispersion Science and Technology, 9 (2), 149-169 (1988) and Speciality Chemicals, 376-378 (1991).

The present invention is based on the discovery that certain polymers can function as hydrotropes.

Summary of the Invention

According to the present invention there is provided an aqueous composition, comprising electrolyte, surfactant and polymeric hydrotrope.

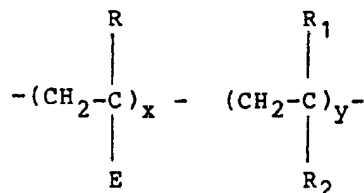
The polymer may be a homopolymer or a copolymer, and preferably comprises hydrophilic and hydrophobic monomers.

The hydrophilic monomer is preferably selected from group: acrylic acid and substituted acrylic acids, eg. methacrylic acid, maleic acid and half-esters thereof, crotonic and itaconic acids and other alkene carboxylic acids and their derivatives, carboxylated styrene, sulphonated styrene, ethylene sulphononic acid, and certain nitrogen-based monomers eg acrylamide, vinyl pyrrolidone, and mixtures of such hydrophilic monomers.

The hydrophobic monomer is preferably selected from the group: styrene and substituted styrenes, eg. alpha-methyl styrene, alpha-olefins, eg. C<sub>12</sub>-alpha-olefin, vinyl ethers, eg. butyl vinyl ether; allyl ethers, eg. butyl allyl ether; unsaturated hydrocarbons, eg. ethylene, propylene, cyclohexene and dienes, eg. 1,6 hexadiene, divinyl benzene, cyclohexadiene, esters of acrylic and substituted acrylic acids, eg. butyl acrylate, ethyl acrylate, methyl methacrylate, esters of other ethylenically unsaturated carboxylic acids, eg. of itaconic acid, crotonic acid, esters of ethylenically unsaturated sulphononic acids eg. alkyl styrene sulphonates, alkyl and aryl vinyl sulphonates and sulphates, alkyl and aryl allyl sulphonates and sulphates. Such hydrophobic moieties may also be introduced into the polymer by chain transfer agents and initiators, eg. mercaptans, eg. dodecyl mercaptans, and peroxides and azo initiators, eg. dialauryl peroxide, AZBN (azobisisobutyronitrile). Mixtures hydrophobic monomers may also be used.

A single monomer with both hydrophilic and hydrophobic properties may also be used.

The polymer preferably has the following formula:



where

E is a hydrophilic functional group;

R is H or a lower (C<sub>1</sub>-C<sub>10</sub>) alkyl group or is a hydrophilic functional group;

R<sub>1</sub> is H a lower alkyl group or an aromatic group;

R<sub>2</sub> is H or a cyclic, alkyl or aromatic group.

One preferred polymer comprises acrylic acid and styrene, possibly with minor amounts of dodecylmercaptan (DDM). Acrylic acid is preferably present in an amount in the range 50-80% by wt, the styrene is preferably present in an amount in the range 20-50% by weight and DDM is preferably present in an amount up to about 1% by weight, eg 0.1 - 1% by weight.

A particularly preferred polymer comprises 50.81 wt% acrylic acid, 48.93 wt% styrene, 0.26 wt% DDM, with a molecular weight of about 1,000 and substantially no cross-linking. This polymer is found to be very versatile and to have a wide range of uses and applications.

Another preferred polymer comprises 54 wt% methacrylic acid and 46% styrene, with a molecular weight of about 100,000 and substantially no cross-linking. Such a polymer is found to be hypochlorite-stable and to be an effective thickener in hypochlorite bleach.

For most applications the polymer is preferably substantially non cross-linked, although a degree of cross-linking can be tolerated.

The polymer typically has a molecular weight of between about 1000 and 1,000,000. For many purposes polymers with molecular weights at the bottom end of the range are preferred, as these generally make better hydrotropes. For example, a polymer with a molecular weight of about 1000 is found to be very versatile and useful in a wide range of applications. Polymers with higher molecular weights, eg about 100,000, also function well as hydrotropes and may additionally perform a thickening function which may be desirable in certain applications, eg production of thickened bleach compositions.

Suitable polymers can be readily made in conventional manner, eg by emulsion or solution polymerisation, and are preferably in the form of low viscosity aqueous solutions or powders.

Suitable polymers are also commercially available, eg acrylic acid/styrene copolymers such as those sold under the Trade Name Joncryl, ethylene/acrylic acid copolymers such as those sold under the Trade Name Primacore, polystyrene sulphonate homopolymers such as those sold under the Trade Name Versa, eg Versa TL502, methacrylic acid/ethyl acrylate copolymers such as those sold under the Trade Name Alcogum, eg Alcogum L11, and various predominantly acrylic acid/ester copolymers such as those sold under the Trade Names Acrysol ICS1, Rheovis CRX and Viscalex HV30.

The polymer is present in an appropriate amount to achieve desired results, such as particular desired composition properties, and suitable amounts can be readily determined by experiment. Typically amounts in the range 0.1 to 15% by wt as active material are suitable, preferably 0.5 to 10% by wt.

Formulations to which the hydrotrope may be added may contain a single surfactant or a mixture of surfactants selected from a wide range, including the following: alkyl ether sulphates, eg. lauryl ether sulphate, such as those sold under the Trade Names Empicol ESB3 (Na salt with 2 ethylene oxide (EO) units), Empicol MD (Na salt, 4EO), Empimin KSN and Perlankrol ESD (both Na salt, 3 EO), alcohol sulphates, eg lauryl alcohol sulphate, such as those sold under the Trade Names Empicol LZV and Empicol LX28, tallow alcohol sulphates, such as those sold under the Trade Name Empicol TAS30, alkyl benzene sulphonates, eg that sold under the Trade Name Nansa SL30, paraffin sulphonates, eg that sold under the Trade Name Lutensit A-PS, alkyl phenol ether sulphates, eg. those sold under the Trade Names Perlankrol PA conc, Perlankrol SN, and Perlankrol RN75, alcohol ethoxylates, eg. those sold under the Trade Names Dobanol 91-6, Ethylan CD 916, Emplian KC8, Synperonic A3 (3EO) and Synperonic A7 (7EO), nonylphenol ethoxylates, eg that sold under the Trade Name Ethylan BCP, sodium carboxylates (soaps) (salts of fatty acids), manufactured from fatty acids such as those sold under the Trade Names Prifac 7908 and Prifac 6920 by neutralisation of the acid with a base eg sodium hydroxide or triethanolamine; alkyl ether carboxylates, eg that sold under the Trade name Olin CS1, alkyl polyglucosides, eg. those sold under the Trade Name Plantaren, EP/PO block copolymers, eg those sold under the Trade Names Plurafac, Triton, and Monolan PC, alkyl diphenyloxide sulphonate, eg. that sold under the Trade Name Dowfax 3B2, fatty acid amides, eg those sold under the Trade Names Empilan CME/CDE, acyl sarcosinates, alkyl taurides, sulposuccinates, eg that sold under the Trade Name Empimin OT, alpha-olefin sulphonates, phosphate esters (alkyl and/or aryl), eg those sold under the Trade Name Phospholan, ethoxylated fatty acids, triethanolamine lauryl sulphate, eg that sold under the Trade Name Empicol TL40, triethanolamine alkyl benzene sulphonate, eg that sold under the Trade Name Nansa TS50, sodium alpha olefin sulphonate, eg that sold under the Trade Name Nansa LSS38.

Suitable mixtures of surfactants are generally found to give good results.

Surfactant is conveniently present in an amount in the range 0.5 to 80% by wt active matter, typically about 3% by wt active matter.

The electrolyte may comprise one or more of a wide range of materials, including salts of complex phosphates, silicates, hypochlorites, carbonates, hydroxides, organic and mineral acids, and sequestrants such as ethylenediaminetetracetic acid and sodium nitrilotriacetate.

Electrolyte is typically present in an amount in the range 1 to 30% by wt as active material.

The composition may include optional ingredients such as, buffer, fragrance, colouring agents, whiteners, solvents and builders, to improve the physical properties of the product of its performance during use or for aesthetic reasons.

Suitable proportions of all ingredients may be readily determined by experiment for any particular formulation.

The invention can provide substantially clear, stable, homogenous, isotropic, solutions, that are desirably stable over a range of temperatures, eg -5 to 50°C.

Without wishing to be bound by any explanation, the applicants believe that hydrophobic groups of the polymer are, according to their hydrophobicity, incorporated into either the region between the surfactant head-groups in a micelle (commonly called the palisade layer), or into the lipophilic interior of the micelles. Replussions between anionic groups in the highly charged polymer backbone decrease the extent to which surfactant molecules can pack into energetically favourable conformations to give liquid crystalline phases. Polymeric hydrotropes therefore act as efficient solubilizers for such surfactants.

Use of polymeric hydrotropes, in preferred embodiments of the invention at least, can have certain advantages compared with use of conventional hydrotropes, including the following:

1. low foaming properties;
2. good surfactant solubilising characteristics;
3. chemical stability;
4. ease of handling;
5. cost effective;
6. substantially free of nitrosamines commonly associated with compositions using nitrogen-based hydrotropes or solubilisers, such as amine oxides.

Further, polyacrylic acid copolymers are known to be good dispersants, scale inhibitors and crystal modifiers and show favourable toxicology.

It is found that the polymeric hydrotrope may act to increase the rate of dissolution of surfactant in water: this is a useful property in detergents.

The hydrotrope can also act as a dispersant and an emulsifier, and can reduce soil redeposition, a useful property in laundry products (liquids and powders).

Compositions in accordance with the invention can be embodied as a wide range of household, institutional and industrial cleaning products, particularly fabric and hard surface cleaning products, such as heavy and light duty liquid detergents, fabric washing detergents, automatic and manual dishwashing detergents, caustic oven cleaners (where the hydrotrope acts to solubilise surfactant and thicken), thickened bleach compositions (with the hydrotrope performing a thickening function), toilet cleaners, multi-surface cleaners etc.

The invention will be further described, by way of illustration, in the following examples and by reference to the accompanying drawings, in which:

Figure 1 is a graph of inverse cloud point of the alcohol ethoxylate surfactant Ethylan CD916 indicating the effect of various additives;

Figure 2 is similar to Figure 1 for the anionic surfactant Nansa SL30;

Figure 3 is a graph of % hydrotrope required to solubilise 2% alcohol ethoxylate surfactant into a caustic solution of given concentration;

Figure 4 is a series graphs of viscosity and % transmission for various mixtures, with results for viscosity shown by solid bars and those for % transmission shown by hatched bars; and

Figure 5 is a dispersant demand curve for 53.8% red iron oxide slurry, plotting viscosity (mPa.s) versus % polymer 1 on pigment.

#### Example 1. Manufacture of Acrylic Acid/Styrene/DDM

A substantially non cross-linked polymer (referred to as polymer 1) of acrylic acid (50.81% wt), styrene (48.93% wt) and DDM (0.26% wt) with a molecular weight of about 1,000 (characterised by GPC compared with polyacrylate standards) was made on a pilot scale by convention solution polymerisation techniques. The materials used are as follows:

	<u>Reactor charge</u>	<u>Grms</u>	<u>Remarks</u>
	Deionised water	2400	Heat to reflux (86°C)
5	Isopropyl alcohol	2400	
	<u>Monomer (slow-add)</u>		
10	Acrylic acid	2160	Add over 3 hrs.
	Styrene	2080	
	DDM	11	
15	<u>Catalyst (slow-add 1)</u>		
	t-butyl hydroperoxide	400	Add over 3½ hrs.
	Isopropyl alcohol	200	
20	Deionised water	200	
	<u>Catalyst (slow-add 2)</u>		
25	Formasul	160	Add over 3½ hrs.
	Deionised water	700	
	Hold one hour		
30	<u>Distillation</u>		
	Azeotrope	4750	Remove with vacuum
35	<u>Neutralization</u>		
40	47% Caustic soda soln.	2000	Add with cooling
	<u>Dilution</u>		
45	Deionised water	8000	Add before neutralisation to help cool.

50 The procedure used was as follows:

The initial charge of deionised water and isopropyl alcohol was added to a 15 litre stainless steel reactor fitted with a lid which has inlet ports for an agitator, water condenser and for the addition of monomer and initiator solutions. The reactor contents were heated to reflux (approximately 86°C).

55 At reflux continuous additions of the monomer and initiator solutions were added to the reactor concurrently with stirring over 3 hours and 3.5 hours, respectively. At the end of the initiator slow-add the reaction temperature was maintained at reflux for a further 1 hour to eliminate any unreacted monomer.

After the 1 hour the alcohol cosolvent was removed from the polymer solution by azeotropic distillation under vacuum. During the distillation deionised water was added to the reactor to maintain reasonable polymer

viscosity:

Once the distillation stage had been completed the polymer solution was cooled to less than 60°C and a solution of a base, such as sodium hydroxide solution, was added maintaining the reactor temperature below 60°C to yield a polymer solution having a final pH of approximately 7.

5 The resulting product was an aqueous solution of acrylic acid/styrene/DDM co-polymer with the following typical properties:

Solids	= 35.4
pH	= 7.0
Viscosity (Brookfield 2/20)	= 820mPas

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#### Example 2 Measurement of Inverse Cloud Point

There are several tests described in the prior art to determine the efficiency of a hydrotrope. One such test that indicates if a chemical can perform as hydrotrope is to establish whether the material will raise the "inverse cloud point" of an aqueous solution of a nonionic surfactant such as an alcohol ethoxylate.

15 A mixture containing 1% w/w active hydrotrope and 5% w/w active alcohol ethoxylate (C<sub>9-11</sub>/6EO)(Ethylan CD916) in deionized water was made, and its pH adjusted to 10 with dilute caustic soda solution.

100ml of this solution was placed in a test tube and the test tube warmed gently in a bath of hot water. The liquid mixture within the test tube was stirred continuously with a thermometer, and the temperature at which cloudiness or haziness of the mixture occurs noted. This temperature is known as the "inverse cloud point" of the mixture; it reflects the onset of insolubility of the surfactant in the aqueous medium. Care was taken not to warm the system too quickly.

Figure 1 illustrates the effects of some common hydrotropes and other materials on the inverse cloud point of Ethylan CD916. This figure includes data for various controls (shown in solid bars), various known hydrotropes (shown in dotted bars) and also polymer 1 (shown in a hatched bar).

25 The onset of insolubility of this class of surfactants occurs at elevated temperatures and hydrotropes tend to increase the cloud point.

#### Example 3

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Experiments similar to those of Example 2 were performed surfactant Nansa SL30 (which is a linear alkyl benzene sulphonate) by various selected commercially available hydrotropes and also polymer 1.

Mixtures were made up containing 5% w/w Nansa SL30 and 1% w/w active hydrotrope in deionised water, with pH adjusted to 10 with NaOH. Aliquots of solution were cooled slowly in an ice/salt water bath until they clouded, and this temperature was noted. Care was taken not to supercool the solution.

35 The results are shown graphically in Figure 2, which includes results for controls (shown in solid bars), commercially available hydrotropes (hatched bars) and polymer 1 (dotted bar). Figure 2 shows that the performance of polymer 1 is comparable to that of certain selected commercially available hydrotropes and that it assists in solubilising the surfactant at lower temperatures. Hydrotropes tend to decrease the cloud point of this class of surfactants.

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#### Example 4. Solubilization of Dobanol 91-6 into Water/Caustic Soda

Solutions containing 5, 10 15 and 20% w/w dry NaOH were prepared on 1000g scale - example formulation on a:

45 15% w/w active NaOH (47% S/C) - 319.1g  
2% Dobanol 91-6 - 20g  
Water to 100% - 660g

Dobanol 91-6 is an alcohol ethoxylate (C<sub>9-11</sub>/6EO) which is chemically very similar to Ethylan CD916.

50 Solutions to 15% w/w active hydrotrope, 2% Dobanol 91-6 and water were then prepared as above.

A 100g aliquot of the caustic mixture under test was weighed into a 250ml sample bottle and placed under stir on a magnetic stirrer plate. The mass of the bottle and aliquot was also recorded. The hydrotrope mixture was then placed in a burette and the caustic mixture titrated against the hydrotrope mixture until the solution became clear; this point was deemed the end point. The mass of the sample bottle and contents was then recorded and thus the amount of hydrotrope and final caustic level calculated. A plot of percent NaOH on the ordinate against percent hydrotrope on the abscissa was produced in order to determine the hydrotropic performance of the test sample.

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Tests were carried out with 3 materials, sodium xylene sulphonate (NXS) (crosses in boxes), phosphate ester (Phosphalan PHB14) (double crosses), and polymer 1 (crosses), and the results are illustrated graphically in Figure 3. In this figure, the lines indicate the point at which visual clarity is maintained, with the regions to the left of the lines indicating cloudy solutions while those to the right of the lines indicate clear solutions.

This data shows that polymer 1 exhibits improved efficiencies at solubilizing an alcohol ethoxylate in caustic soda solutions of 1 - 12% w/w caustic compared with the phosphate ester hydrotrope.

In comparison with another commonly used hydrotrope, sodium xylene sulphonate, the polymer shows improved efficiency (ie lower dose level of hydrotrope) up to and above 15% w/w active caustic soda.

Polymer 1 thus functions effectively as a hydrotrope, and of the three materials tested in the Example, it is the best performer at NaOH concentrations below about 12%.

Polymer 1 is thus an effective hydrotrope and can be used in a range of cleaning formulations. Examples of typical formulations are as follows:

### Heavy Duty Liquid Detergent

% w/w active		
30%	Dobanol 25-7	60g
10%	LABS	66.7g
1%	Sodium carbonate	2g
3.5%	Ethanol	7g
1%	KCl	2g
2%	Polymer 1	11.3g
to 100%	Water	49g

### Caustic Oven Cleaner

% w/w active		
1%	Ethylan CD91-6	4.2g
8%	Sodium hydroxide	16g
1%	Polymer 1	5.6g
to 100%	Water	176.3g

### Laundry Prespotter

% w/w active		
3.9%	Dobanol 25-7	7.8g
2.1%	Empilan KB3	4.2g
0.5%	EDTA Na <sub>4</sub> salt	1g
8.85%	Polymer 1	50g
to 100%	Water	137g

A substantially non-cross linked polymer (referred to as polymer 2) of methacrylic acid (54% wt) and styrene (46% wt) with a molecular weight of about 100,000 (characterised by GPC compared with polyacrylic stan-

dards) was made by conventional emulsion polymerisation techniques.

This polymer also functions as a hydrotrope and is also found to be hypochlorite-stable and so to be useful in thickening hypochlorite bleach compositions.

5 Example 5. Behaviour of polymer 2 in 5% Sodium Hypochlorite

In order to test the behaviour of polymer 2 in 5% sodium hypochlorite, various mixtures were made up as follows (all % are w/w active matter):

1.

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Empicol MD	2%
Empicol ESB3	1%
Polymer 2	1.74%
NaOCl	5%

15

2.

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Empicol MD	2%
Empicol ESB3	1%
NaOCl	5%

25

This mixture was non-homogeneous and separated overnight.

3.

30

Polymer 2	1.74%
Deionised water	balance to 100%

4.

35

Polymer 2	1.74%
NaOCl	5%

In all cases the pH was adjusted to 13 with NaOH.

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For each mixture the % transmission at 500nm was tested to give an indication of clarity, and the viscosity at 3/20 rpm was also tested. The results are shown graphically in Figure 4, with results for the mixtures above given in correspondingly numbered bars.

45

It can be seen from Figure 4 that polymer or surfactant alone in hypochlorite (mixtures 4 and 2, respectively) give poor results in terms of both clarity and viscosity. However, mixtures of polymer, surfactant and hypochlorite (mixture 1) give very good results in terms of both clarity and viscosity. A synergistic effect is thus occurring between the polymer and surfactant.

Example 6. Thickened bleach composition using polymer 2

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A thickened 5% hypochlorite formulation was made by mixing the following ingredients:

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Component	Use Level (%)
Empicol MD (30% active)	2
Empicol ESB3 (27.5% active)	1
Polymer 2 (31% active)	1.74
Sodium hypochlorite (14% active)	5
Fragrance	0.3%
Water	100%

pH was adjusted to 13 with 4% caustic.

The resulting composition had a clear aspect and a viscosity (Brookfield) 3/20 rpm of 275 mPas. and is suitable for use eg as a domestic multi-surface cleaning product.

Example 7

Experiments were carried out to quantify the effect of polymer 1 on the rate of dissolution of two surfactant types:-

1. A seven mole ethoxylated alcohol, an example of which is Synperonic A7 (ex ICI Chemicals and Polymers).

2. A three mole ethoxylated alcohol, an example of which is Synperonic A3 (also ex ICI).

The surfactant Synperonic A7 forms two types of liquid crystal phase on dilution with water. Between about 70 and about 50% w/w surfactant in water, a lamellar liquid crystalline system is formed. However, between 50 and 40% w/w in water, the surfactant forms an immobile gel, called the hexagonal phase. It is the formation of the latter around droplets of neat surfactant in water which retards the dissolution. Commercially available hydrotropes are able to break up or prevent the liquid crystalline phases from forming.

The surfactant A3 forms only lamellar liquid crystalline structures and is not truly soluble in water. Again, commercial surfactant-based hydrotropes are particularly efficient at disrupting the molecular packing in lamellar phases.

All dissolution measurements were made using deionized water containing  $0.8\text{g l}^{-1}$  of sodium carbonate maintained at  $40^{\circ}\text{C}$ .

The following method was used:

1. One litre of deionized water was warmed to  $40^{\circ}\text{C}$  and  $0.8\text{g l}^{-1}$  of anhydrous sodium carbonate added to model the typical levels of electrolyte in a fabric washing liquor. The electrolyte solution was stirred gently using a blade stirrer.

2. To 15g of melted nonionic surfactant, 0.225g of dry polymer was added. All the synthetic and starch-based polymers used in this experiment were dry powders with typically less than 10% moisture content. The level of polymer used as a percentage weight basis of surfactant was 1.5%.

3. A clean, dry plastic spoon that had been modified by bending the handle so that it was at right angles to the bowl, was weighed on a four figure balance and then 1g of (surfactant + polymer) mixture pipetted into the bowl.

4. The spoon was immersed into the water, held in place by a clamp and the time taken for the surfactant mixture to dissolve completely observed.

5. When dissolution had occurred, the spoon was removed, oven dried at  $60^{\circ}\text{C}$  and reweighed. In every case, the residual mass of surfactant was less than 0.03g and therefore it was concluded that the dissolution process was complete.

6. Two controls were used. These were the measurement of surfactant dissolution in the absence of polymeric additives and the measurement of the rate of dissolution of each surfactant containing a cold water soluble powdered maize starch. The latter was included to show that increases in the rate of dissolution of surfactant containing powdered polymer were not due only to the natural dispersing action of the polymer crystals.

Results are shown in the following table.

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Surfactant	Polymer at 1.5% on surfactant	Time of complete dissolution minutes
A7	None	1.45
	Polymer 1	1.17
	Sodium xylene sulphonate powder	1.01
	Waxy maize starch	1.33
A3	None	13.37
	Polymer 1	11.00
	Sodium xylene sulphonate powder	7.03
	Waxy maize starch	12.00

It can be seen from the results that:

1. Incorporation of a powdered polymer with relatively little functionality eg starch can increase the rate of dissolution of the surfactant synperonic A7, possibly by a dispersion mechanism.
2. Polymer 1 is effective at increasing the rate of dissolution of synperonic A7.
3. Either competition for water between COOH groups and the synperonic A7 surfactant ethylene oxide units or interactions between these groups gives a similar effect.
4. Polymer 1 increases dissolution rate of Synperonic A3 but not to the same extent as sodium xylene sulphonate.

The incorporation of polymer 1 into nonionic ethoxylated surfactants has thus been shown to increase their rate of dissolution in water. However, it is not clear from this work whether this is attributable to the amphiphilic nature of the polymer or is a result of the competition between the polymer carboxylic acid functions and the ethylene oxide groups of the surfactant molecules for water.

#### Example 8

Experiments were performed with polymer 1 included in a zeolite detergent formulation to test the activity of polymer 1 as an antiredeposition agent during fabric washing tests.

The detergent had the following composition:

25%	Zeolite 4A (ex Degussa)
4%	Na silicate 2.4:1
10%	Soda ash
9%	Na LABS
1%	Neodol 25-9
q.s.	Sodium sulphate
	Polymer 1 as indicated

NaLABS is a sodium C<sub>12-14</sub> linear alkyl benzene sulphonate surfactant. Neodol 25-9 is a C<sub>12-C<sub>15</sub></sub> synthetic alcohol ethoxylated with 9 moles of ethylene oxide, available from Shell Chemicals and also known under the Trade Name Dobanol.

Various types of fabric (100% cotton, 50% cotton/50% polyester) and 100% polyester were soiled with a polar clay soil comprising 0.1g 4:1 redart clay: black iron oxide. The fabric was washed in 1% detergent at 40°C for 10 minutes and rinsed for 5 minutes. Measurements were made of the amount of white light reflected from the surface of the washed fabric.

Results are given below.

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	Polymer	Hardness ppm CaCO <sub>3</sub>	Reflective Total R		
			Cotton	50:50 Cot:Poly	Polyester
5	None	100	45.6	54.6	50.5
	Polymer 1	100	50.4	58.9	58.5
	Polymer 1	100	51.5	59.5	59.2
10	None	300	46.0	49.8	55.7
	Polymer 1	300	50.7	54.5	63.8
	Polymer 1	300	51.5	54.3	57.6
15	Least significant difference at 90% confidence		0.8	0.5	1.1

The measurements of R (reflective) above indicate the proportion of white light reflected from the surface of the washed fabric and are an indication of "whiteness", thus the higher the value of R the less soil redeposited.

Polymer 1 thus shows some activity as an antiredeposition agent against a polar clay soil, although no such effect was observed in similar tests using non-polar soils.

#### Example 9

A red iron oxide pigment with a high dispersant demand was used to illustrate the dispersant action of polymer 1 compared to sodium xylene sulphonate.

350g of pigment were slurried into 300g of deionized water at pH6. An aliquot of polymer 1 or sodium xylene sulphonate was added to the slurry and the slurry high-shear mixed at 2000rpm for 15 minutes. After a two minute period, the viscosity of the slurry was measured on a Brookfield RVT viscometer using spindle 4 at 100rpm. A further aliquot of polymer solution or sodium xylene sulphonate was then added and the slurry mixed at high shear for a further 10 minutes. The viscosity of the slurry was measured and the addition of polymer or sodium xylene sulphonate followed by mixing was repeated until the viscosity of the slurry started to rise.

Results are shown in Figure 5. The excellent dispersant action of polymer 1 is evident from the dispersant demand curve. The minimum in the curve for the slurry dispersed with polymer 1 occurs at a low dose and at a low viscosity. In contrast, the sodium xylene sulphonate did not disperse the iron oxide and a highly viscous paste was formed. Furthermore, the performance of polymer 1 is comparable to that of commercially used dispersants such as homopolymers of acrylic acid, eg Narlex LD31.

#### Example 10

The ability of polymer 1 to emulsify oils of various hydrophobicity was determined by conducting experiments using two water-insoluble fragrances, a general all-purpose household product fragrance and a skin-care fragrance.

A 1g portion of one fragrance was dispersed into deionized water using high shear mixing such that the level of fragrance dispersed was 0.5% by weight.

The dispersion was stabilized with either 1,2,3 or 4% by weight of active polymer 1.

In every case, opaque emulsions were formed which were stable to coagulation, although creaming did occur. The emulsions remained stable over a 14 day period with no evidence of the formation of a layer of oil on the surface of the aqueous phase, or at the interface of the water and glass container. In contrast, emulsions prepared with sodium xylene sulphonate were less stable to phase separation.

#### Example 11

Polymer 1 was made by an alternative route to the aqueous synthesis of Example 1, involving instead synthesis in non-ionic surfactant. The resulting polymer can be used in non-aqueous systems, where its effect on dissolution rate of surfactants may be useful.

In this alternative route, the surfactant is charged to the reactor and is heated to the reaction temperature, 80-90°C. At this temperature the surfactant should be liquid. At the reaction temperature concurrent feeds of

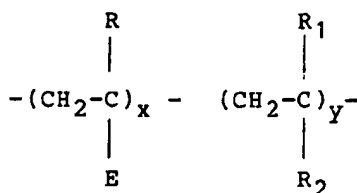
monomer and initiator are added over 3 and 3.5 hours respectively. At the end of the initiator feed the batch is held at the reaction temperature for 1 hour to finish polymerising any unreacted monomer. At the end of the hold the batch is cooled to less than 30°C and transferred to storage.

#### 5 Differences between polymer 1 manufactured by the aqueous and surfactant routes

1. The surfactant route is largely if not totally non-aqueous and this necessitates a change of initiating system. Polymer 1 (aqueous) uses a redox initiating system of tertiary butyl hydrogen peroxide-formasul (sodium formaldehyde sulphonylate). This system requires water for solubility and is therefore unsuitable for the surfactant route. Polymer 1 made in surfactant is typically made with a thermal initiating system. The initiator should ideally be liquid or be soluble in one of the reaction components for ease of use. A suitable initiator would be tertiary butylperoxoate.
2. With the surfactant route no distillation stage is needed. The aqueous route requires removal of the alcohol co-solvent.
3. With the surfactant route no neutralisation stage is needed. The system is non-aqueous and as such has no pH. The polymer 1 made by the aqueous route is neutralised to pH7 for ease of handling.

#### Claims

1. An aqueous composition, comprising electrolyte, surfactant and polymeric hydrotrope.
2. A composition according to claim 1, wherein the polymeric hydrotrope comprises hydrophilic and hydrophobic monomers.
3. A composition according to claim 2, wherein the hydrophilic monomer is selected from group: acrylic acid and substituted acrylic acids, eg. methacrylic acid, maleic acid and half-esters thereof, crotonic and itaconic acids and other alkene carboxylic acids and their derivatives, carboxylated styrene, sulphonated styrene, ethylene sulphonic acid, and certain nitrogen-based monomers eg acrylamide, vinyl pyrrolidone, and mixtures of such hydrophilic monomers.
4. A composition according to claim 2 or 3, wherein the hydrophobic monomer is selected from the group: styrene and substituted styrenes, eg. alpha-methyl styrene, alpha-olefins, eg. C<sub>12</sub>-alpha-olefin, vinyl ethers, eg. butyl vinyl ether; allyl ethers, eg. butyl allyl ether; unsaturated hydrocarbons, eg ethylene, propylene, cyclohexene and dienes, eg. 1,6 hexadiene, divinyl benzene, cyclohexadiene, esters of acrylic and substituted acrylic acids, eg butyl acrylate, ethyl acrylate, methyl methacrylate, esters of other ethylenically unsaturated carboxylic acids, eg. of itaconic acid, crotonic acid, esters of ethylenically unsaturated sulphonic acids eg. alkyl styrene sulphonates, alkyl and aryl vinyl sulphonates and sulphates, alkyl and aryl allyl sulphonates and sulphates.
5. A composition according to claim 1 or 2, wherein the polymeric hydrotrope has the following formula:



where

- E is a hydrophilic functional group;
- R is H or a lower (C<sub>1</sub>-C<sub>10</sub>) alkyl group or is a hydrophilic functional group;
- R<sub>1</sub> is H a lower alkyl group or an aromatic group;
- R<sub>2</sub> is H or a cyclic, alkyl or aromatic group.

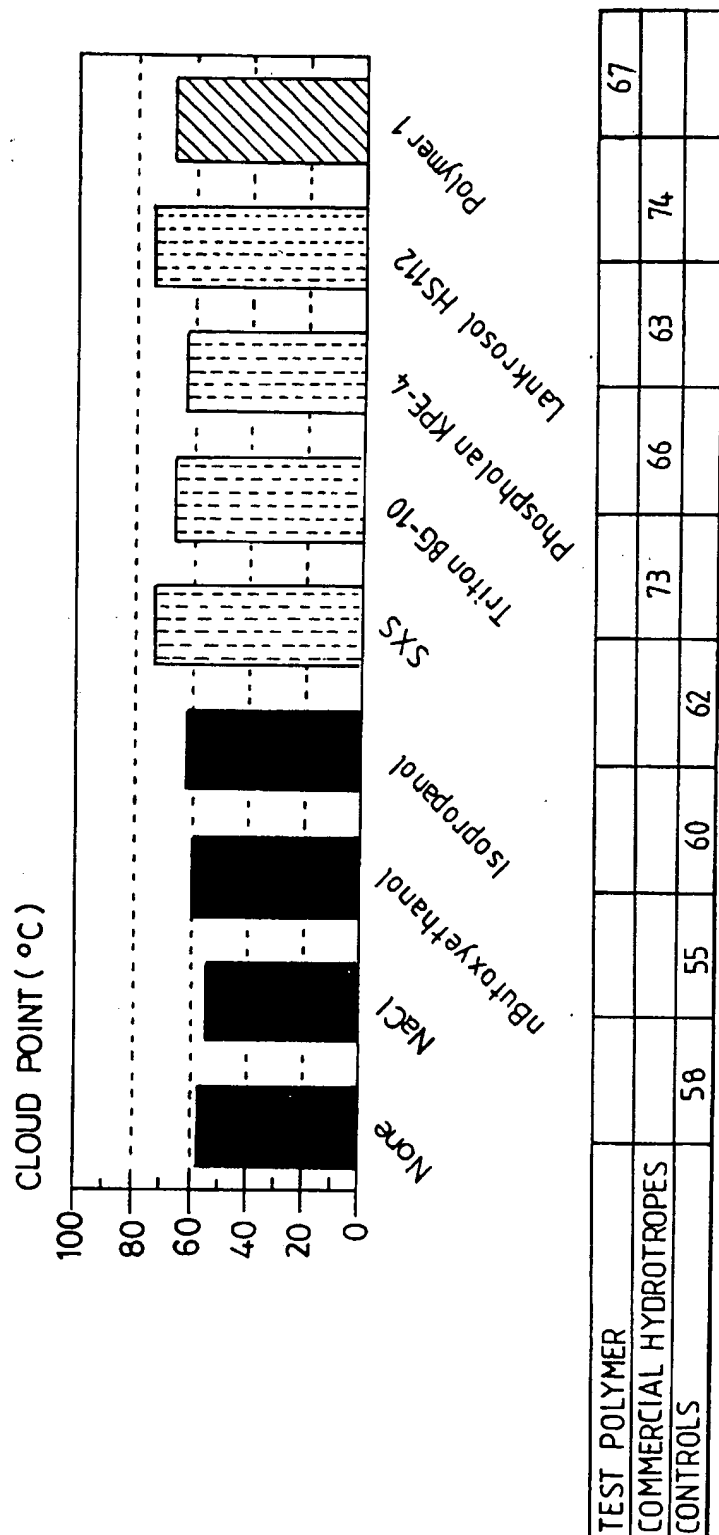
6. A composition according to any one of the preceding claims, wherein the polymeric hydrotrope comprises

acrylic acid and styrene, possibly with minor amounts of dodecylmercaptan (DDM).

- 5 7. A composition according to claim 6, wherein acrylic acid is present in an amount in the range 50-80% by wt, styrene is present in an amount in the range 20-50% by weight, and DDM is present in an amount up to about 1% by weight.
8. A composition according to claim 1, wherein the polymeric hydrotrope comprises 50.81 wt% acrylic acid, 48.93 wt%, 0.26 wt% DDM, with a molecular weight of about 1,000 and substantially no cross-linking.
- 10 9. A composition according to claim 1, wherein the polymeric hydrotrope comprises 54 wt% methacrylic acid and 46% styrene, with a molecular weight of about 100,000 and substantially no cross-linking.
10. A composition according to any one of the preceding claims, wherein the polymeric hydrotrope is substantially non cross-linked.
- 15 11. A composition according to any one of the preceding claims, wherein the polymeric hydrotrope has a molecular weight of between about 1000 and 1,000,000.
12. A composition according to any one of the preceding claims, wherein the polymeric hydrotrope is present in an amount in the range 0.1 to 15% by wt as active material, preferably 0.5 to 10% by wt.
- 20 13. A composition according to any one of the preceding claims, wherein the surfactant comprises one or more surfactants selected from the following: alkyl ether sulphates, eg. lauryl ether sulphate, alcohol sulphates, eg lauryl alcohol sulphate, tallow alcohol sulphate, alkyl benzene sulphonates, paraffin sulphonates, alkyl phenol ether sulphates, alcohol ethoxylates, nonylphenol ethoxylates, sodium carboxylates (soaps) (salts of fatty acids), alkyl ether carboxylates, alkyl polyglucosides, EP/PO block copolymers, alkyl diphenyloxide sulphonate fatty acid amides, acyl sarcosinates, alkyl taurides, sulposuccinates, alpha-olefin sulphonates, phosphate esters (alkyl and/or aryl), ethoxylated fatty acids, triethanolamine lauryl sulphate, triethanolamine alkyl benzene sulphonate, sodium alpha olefin sulphonate.
- 25 14. A composition according to any one of the preceding claims, wherein the surfactant is present in an amount in the range 0.5 to 80% by wt active matter, typically about 3% by wt active matter.
- 30 15. A composition according to any one of the preceding claims, wherein the electrolyte comprises one or more materials selected from the following: salts of complex phosphates, silicates, hypochlorites, carbonates, hydroxides, organic and mineral acids, and sequestrants such as ethylene-diaminetetracetic acid and sodium nitrilotriacetate.
- 35 16. A composition according to any one of the preceding claims, wherein electrolyte is present in an amount in the range 1 to 3% by wt as active material.
- 40 17. A composition according to any one of the preceding claims, further comprising one or more of the following: buffer, fragrance, colouring agents, whiteners, solvents and builders.
- 45 18. A composition according to any one of the preceding claims, in the form of one or more of the following: fabric and hard surface cleaning products, such as heavy and light duty liquid detergents, fabric washing detergents, automatic and manual dishwashing detergents, caustic oven cleaners, thickened bleach compositions, toilet cleaners, multi-surface cleaners.

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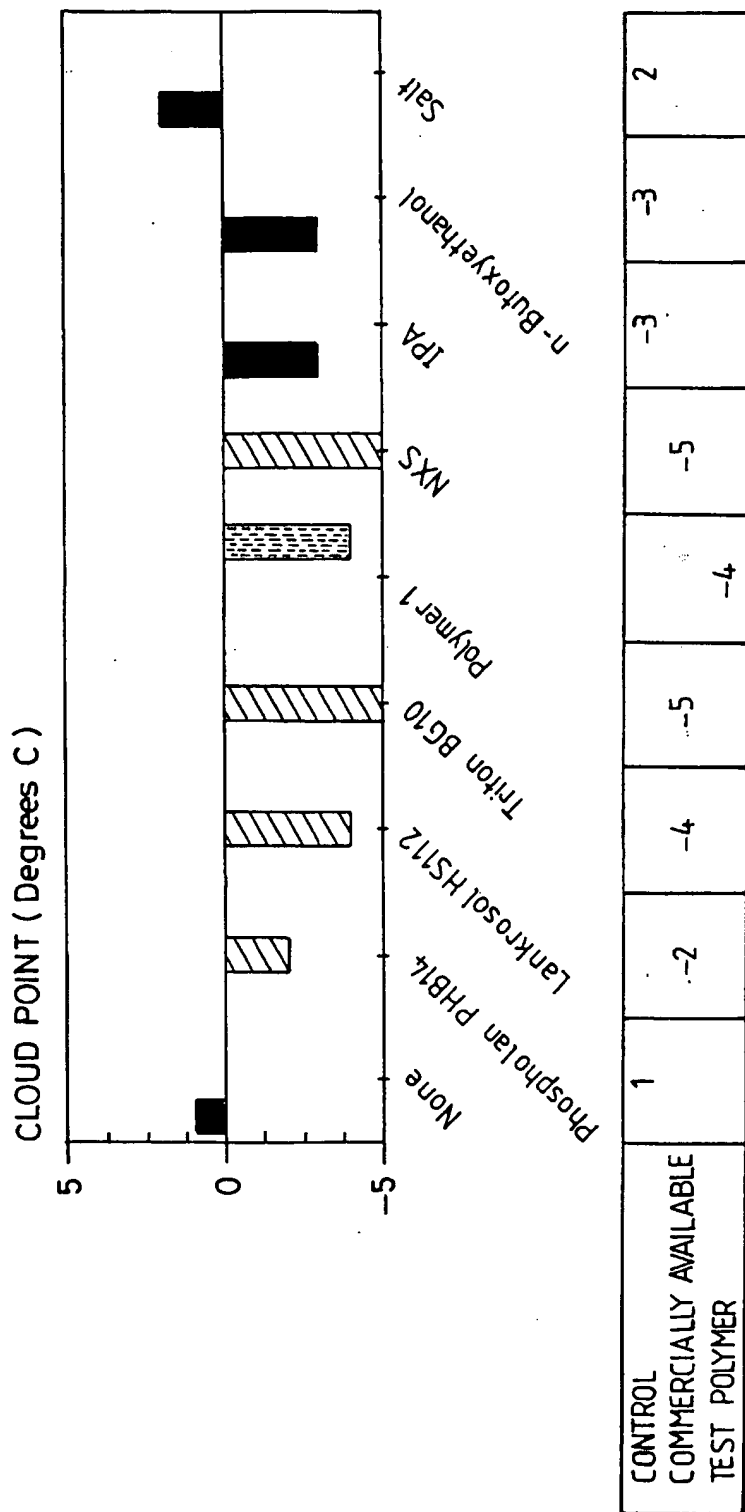


Fig. 2

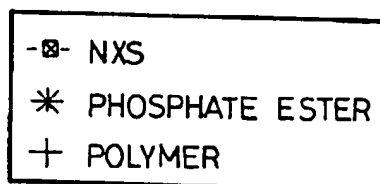
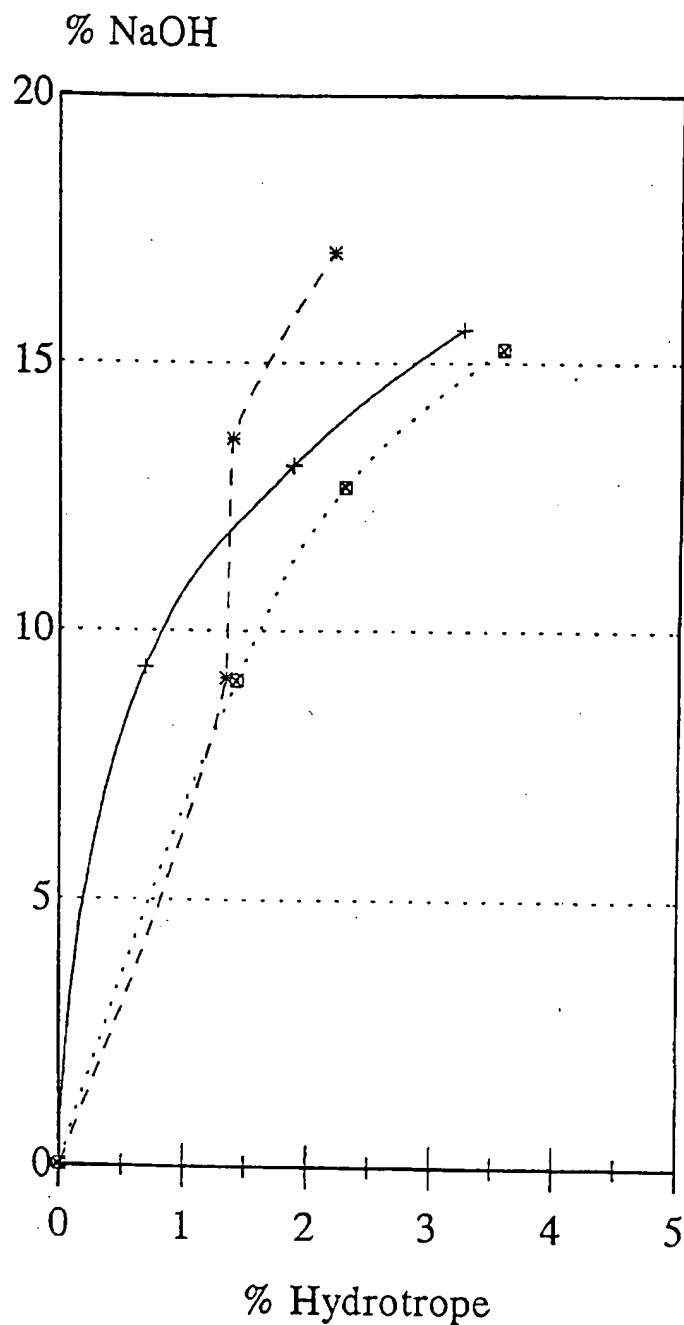


Fig. 3



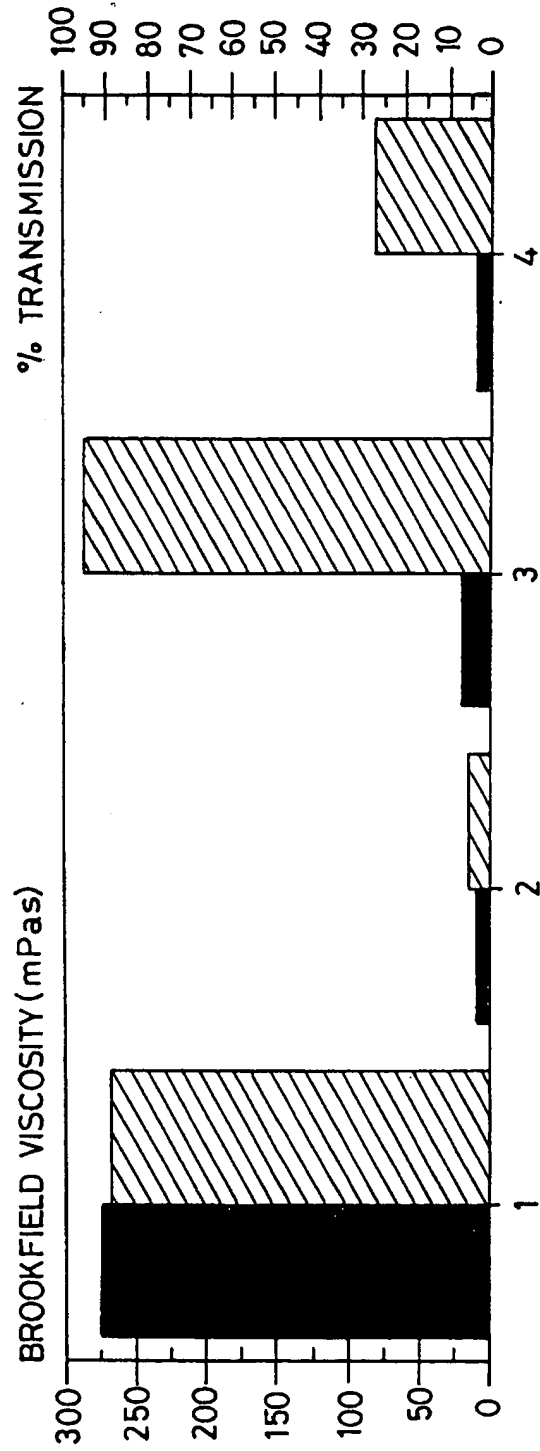


Fig. 4

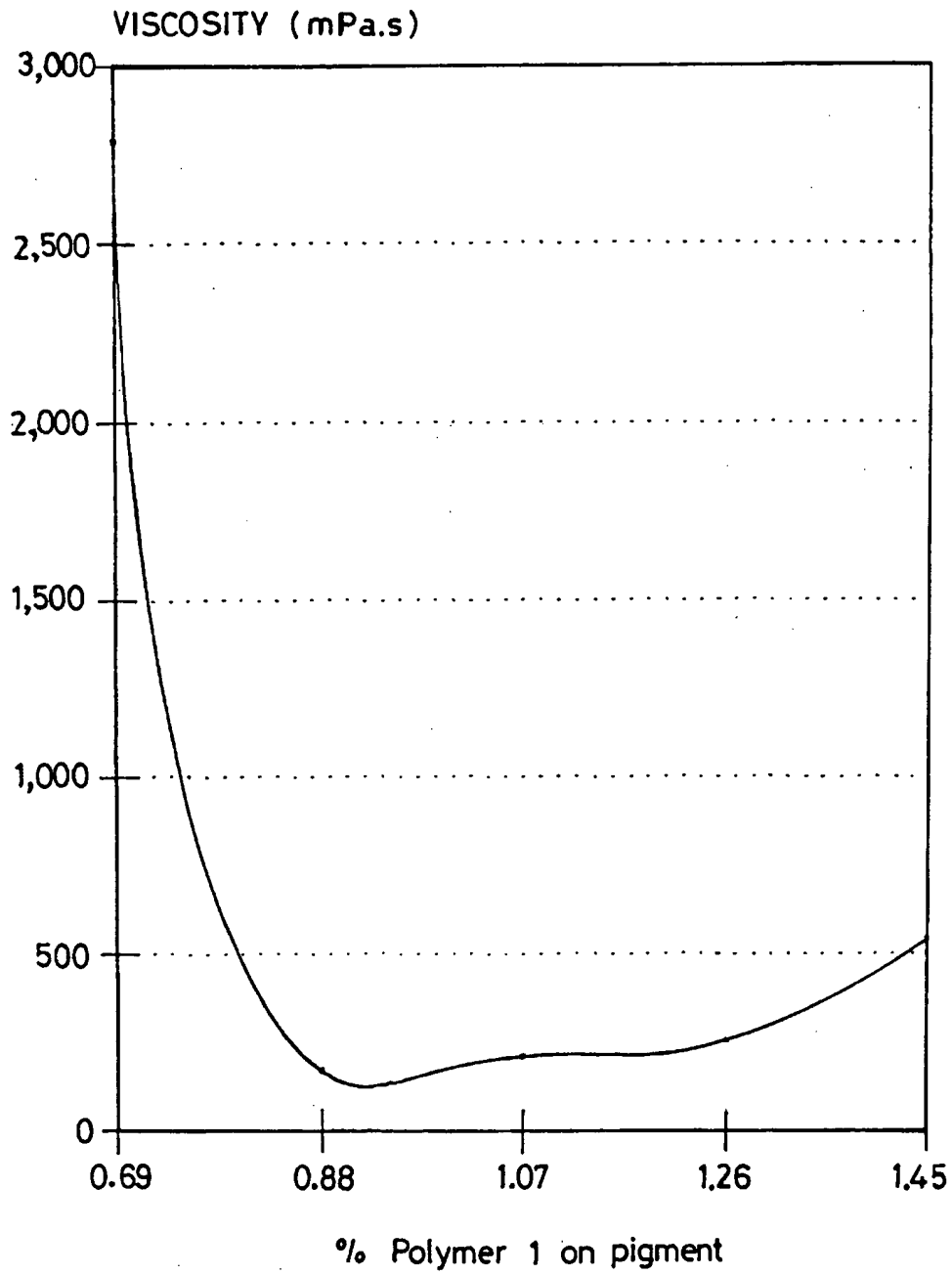


Fig. 5